RECENT DEVELOPMENTS IN ELECTRON TRANSFER REACTIONS

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RÉSUMÉ. — Cet article présente les résultats antérieurs et les développements récents des réactions de transfert électronique. Les résultats expérimentaux les plus nouveaux comprennent la mise en évidence de la diminution de la constante de vitesse des réactions fortement exergoniques, les effets de l'orientation électronique sur les vitesses de réaction, la dynamique des solvants, les étapes primaires en photosynthèse et l'émission lumineuse d'électrons métalliques.

ABSTRACT. — Earlier results and more recent developments in electron transfer reactions are reviewed. The more recent results include inverted behavior, electronic orientation effects on reaction rates, solvent dynamics, early steps in photosynthesis, and light emission from metal electrodes.

Introduction

Research on electron transfer reactions in solution and at electrodes is one of current considerable activity. In this lecture, several aspects of electron transfer theory and experimental tests of its predictions are first summarized. [1] Some recent developments are then reviewed. They include the inverted effect, [1,2] electronic orientation effects, [3,4] solvent dynamical effects, [5-9] the mechanism of some primary steps in the bacterial photosynthetic reaction centers (superexchange vs. intermediate) [10,11], a possible cause of their high efficiency, and light emission from metal electrodes due to electron transfer. [12,13]

Summary of earlier work

In the theory of electron transfer reactions factors such as the changes in molecular structure of the reactants (*e.g.*, changes in bond lengths accompanying the charge transfer between the reactants), changes in solvation of the reactants accompanying the charge transfer, the effect of the driving force of the reaction $-\Delta G^0$ ("standard" free energy of reaction in the prevailing medium), and the work required to bring the reactants together and to separate the products, are treated. [1] An electronic factor which may, in some cases, cause the reaction to be "nonadiabatic" is also relevant. [1]

Detailed theoretical expressions based on these effects have been derived for the rate constant of bimolecular or intramolecular electron transfers in solution and for electron transfers between a reactant and an electrode. Since we have described them in a recent review, [1] we omit a detailed description in the written version of this lecture. We merely note, for clarity in some of the following comments, that the free energy barrier for the reaction ΔG^*, which appears in the expression for the rate constant k, is given in terms of the reorganization quantity λ and ΔG^0 by equation 1. (We have neglected the work terms [1] for notational brevity in this presentation.):

$$\Delta G^* = \frac{1}{4}\lambda(1+\Delta G^0/\lambda)^2. \qquad (1)$$

In the case of an electrode reaction, a similar equation arises, but with ΔG^0 replaced by an activation overpotential and with a λ which is at least one-half the λ for the corresponding reaction in solution, the value depending on the typical distance between the reacting ion and the electrode in the transition state. [1] An expression for these λ's is given in reference [1].

The resulting theoretical expressions for the homogeneous and electrochemical rate constants led to a variety of predictions, which have been the subject of many experimental tests. [1] The predictions include the following: [1]

1) the rate constant k_{12} for reaction between two different redox systems is related to the rate constants of the self-exchange reactions of each of the systems, k_{11} and k_{22}, and to the equilibrium constant K_{12} by the relation $k_{12} \simeq (k_{11}\,k_{22}\,K_{12}\,f_{12})^{1/2}$, where f_{12} is a known function of the k_{ii}'s and K_{12};

2) the rate constant k of a series of similar reactions (*i.e.*, those possessing a similar reorganization term λ) depends on the standard free energy of reaction ΔG^0 or, in the case of an electrode reaction, on the activation overpotential $ne(E-E_0')$, according to the relation

$$RT\,d\ln k/d(-\Delta G^0) \simeq 0.5(1+\Delta G^0/\lambda);$$

3) there is a dependence of $\ln k$ on the dielectric properties of the solvent $(D_{op}^{-1}-D_s^{-1})$ with a known slope, in the absence of specific solvent-solute interactions;

4) the rate constant for the electrochemical exchange current at an electrode k_{el} (zero activation overpotential) and for the corresponding self-exchange reaction in homogeneous

solution k_{ex} are related according to $k_{el}/Z_{el} \leqq (k_{ex}/Z_{ex})^{1/2}$, where the Z's denote collision frequencies with the electrode (Z_{el}) and in solution (Z_{ex}) (the equality sign occurs when no adsorbed solvent layer separates the reactant from the electrode);

5) with increasingly negative ΔG^0, k increases as $-\Delta G^0$ gets larger, which is the normal behavior, but when the driving force $-\Delta G^0$ is very negative, k decreases as $-\Delta G^0$ gets larger (the "inverted region"), for a series of homogeneous reactions of similar λ; the maximum in k occurs at $-\Delta G^0 = \lambda$;

6) the k's can be calculated in terms of bond lengths' (angles') changes, sizes and charges of reactants, dielectric properties of the solvent and, in the particular case of nonadiabatic reactions, an electron transfer matrix element;

7) there is a quantitative expression relating the free energy barrier of the reaction and the position of the analogous charge transfer spectral absorption maximum, as well as a relation to the photoelectric emission spectrum.

The k's mentioned above are, when the work terms are non-negligible, intended to be "work-corrected" k's. Of the various predictions some are not particularly model-dependent, the cross-relation (1), for example, while some, such as the quantitative effect of a non-specific solvent (3), depend on the assumption of a dielectric continuum used for the solvent outside the innermost coordination shell of the reactants. Comparison of the various predictions with the experimental data has been described in the review with Sutin. [1]

Electron transfers are perhaps the simplest of all chemical reactions, when no bonds are broken. The detailed analysis which was possible for them has also served to stimulate use of some of the expressions, such as the cross-relation (1), with some theoretical basis, for the k's for other transfers (proton, hydride, methyl, sulfuryl, phosphoryl). References are given in reference [1].

Recent developments

1. THE INVERTED EFFECT

A prediction which was rather elusive was that of the "inverted" effect (5). Recently, impressive evidence for this effect has been found for an intramolecular charge transfer by Miller, Calcatterra and Closs, [2] who mention also earlier evidence, the study of charge transfer in a glassy matrix. [14] Various possible interfering effects in the case of bimolecular reactions in solutions have been discussed, [15] and further studies of the elusiveness of the effect for bimolecular systems in solutions are warranted. A striking contrast between the behavior of mobile bimolecular systems in solution, where diffusion control can tend to mask the inverted effect, and the intramolecular case have also been described by Miller *et al.* [2] The inverted effect itself is of interest not only in itself but also because of its potential relationship to the high efficiency of photosynthetic systems, a point to which we return later.

2. ELECTRONIC ORIENTATION EFFECTS

Orientation effects on electron transfer reactions have been studied experimentally in several systems, including an investigation of cofacial porphyrins [16] and a study of "jawed" porphyrin-like molecules with their y-axes roughly perpendicular to each other. [17] In the first instance, the electron transfer from an excited magnesium porphyrin to a free base porphyrin was very rapid in the forward direction ($k > 10^{11}\ s^{-1}$) and relatively slow in the reverse direction ($k \sim 10^9\ s^{-1}$), while in the case of the jawed porphyrins the rate was slow in both directions ($\sim 10^9\ s^{-1}$). The first result is consistent with the fast rates estimated for cofacial $(5, \pi) \rightarrow (5, \pi)$ transfers and slow rates for the $(5, \pi) \rightarrow (4, \pi)$ case (because of orthogonality or near orthogonality for the cofacial arrangement). [3] The number 5 or 4 refers to the number of nodes of the electronic wave function about the z-axis of the porphyrin, $(5, \pi)$ being, thereby, the LUMO and $(4, \pi)$ the HOMO for the porphyrin. Calculations for various geometrical arrangements have been given in reference [3], using a quite approximate model of a porphyrin, a spheroidal cavity having a well depth for the electron such that the fall-off of $\ln k$ with distance was appropriate to that found at large distances. The slowness of the back reaction in the cofacial case may also be partly due to the inverted effect, since that reaction has a very negative ΔG^0 and the speed of the forward reaction suggested only a small reorganization barrier λ. Analogous calculations for the orientation appropriate to these in a bacterial photosynthetic reaction center indicated that no large difference in forward and back reactions was expected for the given geometry. [3] In that case, the slowness of the back reaction may be due to other factors, such as the "inverted effect": the nonpolar nature of the environment makes for a small λ, [1] and thereby enhances (*cf.* equation 1) the possibility of having an inverted effect.

In the treatment of electronic orbital orientation effects on electron transfers, there are two types of effects which can occur, "through bond" and "through space" (or "through the solvent medium"). The first of these becomes possible when the two reactants are linked by actual chemical bonds. Distinguishing between the two types is of current interest. The treatment of orientation effects in reference [3] is for a "through space" transfer, while that in reference [4] is "through bond".

3. SOLVENT DYNAMICAL EFFECTS

The study of solvent dynamical effects has been spurred by recent picosecond-type measurements of intramolecular charge transfers in which the intrinsic rate of reaction is so fast that the slow step is the dynamics of the solvent motion itself. [5-9] The solvent relaxation rate is characterized by a "constant charge" dielectric relaxation time, τ_L. Several intramolecular charge transfers in organic solutes in a series of aliphatic alcohols as solvents were studied. [5] The smaller alcohols, (*e.g.*, methanol, ethanol) were dielectrically too fast for the rates to be measured with the equipment used (resolution time $\sim$ 15 ps, but faster response equipment of subpicosecond time is now available). For the other alcohols studied, 1-propanol to 1-decanol, there was agreement between the intramolecular charge transfer rate constant and the reciprocal of τ_L. [5] Questions regarding the choice of τ_L, types of intramolecular charge transfer (two-state *versus* relaxation on a single electronic state curve), non-exponential *versus* single exponential time decay, and the role of the ratio of intramolecular (λ_i) to solvational (λ_0) contributions to λ for each of these topics have been discussed. [6, 8, 9] An approximate expression for the reaction time τ in terms of the usual "equilibrated" rate constant k_e (rate constant when τ_L is small) and τ_L has been given in references [6] and [8] for the case (as seen in reference [9]) that λ_i/λ_0 is small:

$$\tau = k_e^{-1} + F\tau_L \qquad (2)$$

where F is a known function of λ_i/λ_0 and $\Delta G^*/RT$.[6,8] References to other experiments besides those in reference[5] are given in references[6,8] and [9], including an apparently fractional dependence of τ on τ_L in a rather viscous medium.[18] Theoretical calculations leading to a fractional dependence when λ_i/λ_0 is not small are given in reference[9]. The field of solvent dynamics is a rich one and is of much current interest.

4. EARLY STEPS IN BACTERIAL PHOTOSYNTHESIS

The early electron transfer steps in the reaction centers of photosynthetic bacteria have been the subject of many recent experiments, many of them in the picosecond domain. The field was given a major thrust when the crystal structure of one of the reaction centers was determined.[19] Some discussion and review of the kinetics and structure is given in reference[1].

The geometrical arrangement is such that a possible electron transfer route, which yields opposite charges across the membrane, is

$$\underset{\mathbf{I}}{(\mathrm{BChl})_2^*} \xrightarrow{e} \underset{\mathbf{II}}{\mathrm{BChl}} \xrightarrow{e} \underset{\mathbf{III}}{\mathrm{BPh}} \xrightarrow{e} \mathrm{Q} \qquad (3)$$

where the symbols denote, respectively, a photoexcited bacteriochlorophyll dimer, a monomer, a bacteriopheophytin, and a quinone.

Of particular interest is the role, if any, played by the BChl monomer in equation 3. The loss of the electron from **I** occurs in 2.8 ps.[10] A recent determination led to no detection of a BChl^- intermediate.[10] The limits of detectability, however, were perhaps of the order of 15%.

Two possible explanations for not observing BChl^- include: (1) the mechanism of electron transfer from **I** to **III** in equation 3 occurs via a superexchange mechanism, in which case there is only a virtual existence of BChl^-, and not an actual intermediate, and (2) there is an actual intermediate BChl^-, but the rate constant for electron transfer from **II** to **III** is much faster than that for transfer from **I** to **II**.

To distinguish between these two mechanisms, I believe that existing magnetic data can be used: the radicals $(\mathrm{BChl}_2)^+$ and BPh^- are known to interact only very weakly in the reaction center.[20] Based on some preliminary calculations, it does not appear, at present, that this weak coupling is consistent with the extremely rapid loss of the electron from **I** to **II** if a superexchange mechanism prevails.[11] The high superexchange coupling which is assumed to lead to a fast reaction would also lead to a large magnetic coupling. The second alternative mechanism, on the other hand, serves to decouple the two. A detailed treatment is given elsewhere.[11]

The system in equation 3 is of particular interest in the context of the present meeting, because of the high efficiency of the photosynthetic reaction center for utilizing solar energy. In particular, a back reaction to reform $(\mathrm{BChl})_2$ is much slower (~ 10 ns) than the eventual formation of Q^- (~ 200 ps). The explanation of the resulting high efficiency is related to the nature of the electronic coupling between the four entities in equation 3 and to the possibility of an inverted effect in slowing down the highly exothermic reformation of an unexcited $(\mathrm{BChl})_2$. [The reformation of an excited $(\mathrm{BChl})_2$ singlet state is presumably slow by virtue of being energetically uphill, and the formation of an excited $(\mathrm{BChl})_2$ triplet state from the two radicals $(\mathrm{BChl})_2^+$ and BPh^- (or BChl^-) is slow because of the necessary spin realignment discussed by various authors, cited in reference[1].

Perhaps the main features of this highly effective solar utilization scheme in equation 3 include (1) having two reactions **I** → **II** and **II** → **III**, sufficiently downhill that there is a possibility of forming two distant weakly coupled radicals, and (2) having a nonpolar environment in the membrane in the vicinity of **I** and **II**, thereby making the λ in equation 1 small (or the λ in a corresponding quantum mechanical equation small), and so creating the conditions for an "inverted effect" for a given ΔG^0.

5. LIGHT EMISSION FROM METAL ELECTRODES

The phenomenon of the inverse photoelectric effect, namely the emission of light from a metal electrode when the latter is bombarded by high energy electrons, is well-known.[21] Recently, McIntyre and Sass showed that such emission also occurs when an electron is transferred between (to or from) an ion in solution and a metal electrode under a high driving potential.[12] The "threshold" of the light-emission spectrum was linear in the metal solution potential difference. The emission was fairly broad. As the authors remarked, one might be able to extract a reorganization energy λ from the data.

One possibility is to adapt a treatment of intramolecular charge transfer spectra developed in 1965.[22] In the present case, the "molecule" is the ion in solution and the metal. Initially, the electron (or hole) in the ion has a distribution of momenta, in contrast with the electron bombardment case where it is possible to use electrons of given velocity ("k-resolved photoelectric emission").[21] We consider first an assumption, intended to be purely exploratory, that the optical electron transfer matrix element is greatest when the transfer is made to the Fermi level, E_F.

In this case, the value of λ can be determined by measuring the spectral emission maximum, $h\nu_{max}$, for a given value ΔE_m of the metal-solution potential relative to the standard value for that half-reaction:

$$h\nu_{max} = -\lambda + \Delta E_m. \qquad (4)$$

(The sign convention for ΔE_m is such that the higher the driving force ΔE_m, the larger $h\nu_{max}$.) A discussion of the analogous equation for intramolecular charge transfer spectra is given in reference[23].

Equation 4 is, however, inadequate-it predicts more dependence of $h\nu_{max}$ on ΔE_m than shown by the data.[12]

Using a somewhat less restrictive assumption, focusing instead on the high energy side (threshold) $h\nu_{th}$ of the emission band and assuming a Gaussian distribution of solute-solvent energy levels, one finds

$$h\nu_{th} = -\lambda + \Delta E_m + \gamma(4\lambda k_B T)^{1/2}, \qquad (5)$$

where k_B is the Boltzmann constant and γ is a constant whose value depends on the definition of the "threshold" and which is roughly 1.1-1.2 (Equation 5 is still purely exploratory).

Using equation 5 and the data in reference[12], the λ for electron transfer from the benzophenone radical anion in acetonitrile as solvent is calculated to be about 0.4 eV, and that for transfer to the thianthrene cation in the same solvent to be about 0.3 eV.

This value of λ may be compared with the λ found for a homogeneous reaction by Miller *et al.*,[2] who used an equa-

tion analogous to equation 1 to determine λ: the minimum value of ΔG^* and hence the maximum value of the rate constant, when plotted for series of reactants of different ΔG^0, occurs at $-\Delta G^0 \simeq \lambda$. The value of λ for the compounds they studied (for a reacting pair consisting of an aromatic molecule and a quinone) was found, thereby, to be about 1.2 eV in the polar solvent methyltetrahydrofuran and about 0.6 eV in the nonpolar solvent isooctane. Remembering that the λ in the electrochemical case is predicted to be one-half (or larger than one-half) the value for the homogeneous solution case, [1] the value for the polar solvent is seen to be very roughly comparable with that obtained from the photoemission data for this other system.

Values of λ for inorganic ions have been obtained by Delahay *et al.* using photoelectric emission of electrons from ions in solution. [24]

Concluding remarks and acknowledgement

The field of electron transfers has grown enormously from its earlier development, based on isotopic exchange reactions, in the late 1940's and the 1950's. The examples cited above are intended to give some of the more recent developments.

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REFERENCES

[1] Marcus R. A., Sutin N., *Biochim. Biophys. Acta*, 1985, **811**, 265.
[2] Miller J. R., Calcaterra L. T., Closs G. L., *J. Amer. Chem. Soc.*, 1984, **106**, 3047; Closs G. L., Calcaterra L. T., Green N. J., Penfield K. W., Miller J. R., *J. Phys. Chem.*, 1986, **90**, 3673.
[3] Cave R. J., Siders P., Marcus R. A., *J. Phys. Chem.*, 1986, **90**, 1436.
[4] Closs G. L., Private communication.
[5] Kosower E. M., Huppert D., *Chem. Phys. Lett.*, 1983, **96**, 433.
[6] Sumi H., Marcus R. A., *J. Chem. Phys.*, 1986, **84**, 4894.
[7] References to work of Zusman, Alexandrov, Wolynes, Hynes, Ovchinnikova and others are given in reference [6].
[8] Sumi H., Marcus R. A., *J. Chem. Phys.*, 1986, **84**, 4272; Marcus R. A., Sumi H., *J. Electroanal. Chem.*, 1986, **204**, 59.
[9] Nadler W., Marcus R. A., *J. Chem. Phys.*, in press.
[10] Martin J.-L., Breton J., Hoff A. J., Migus A., Antonetti A., *Proc. Natl. Acad. Sci. U.S.A.*, 1986, **83**, 957.
[11] Marcus R. A., *Chem. Phys. Lett.*, in press.
[12] McIntyre R., Sass J. K., *J. Electroanal. Chem.*, 1985, **196**, 199; *Phys. Rev. Lett.*, 1986, **56**, 651.
[13] Marcus R. A., Unpublished.
[14] Miller J. R., Beitz J. V., Huddleston R. K., *J. Amer. Chem. Soc.*, 1984, **106**, 5057.
[15] E.g., Siders P., Marcus R. A., *J. Amer. Chem. Soc.*, 1981, **103**, 748.
[16] Netzel T. L., Kroger P., Chang C. K., Fujita I., Fajer J., *Chem. Phys. Lett.*, 1979, **67**, 223; Netzel T. L., Bergkamp M. A., Chang C. K., *J. Amer. Chem. Soc.*, 1982, **104**, 1952, and references cited therein.
[17] Overfield R. E., Scherz A., Kaufmann K. J., Wasielewski M. R., *J. Amer. Chem. Soc.*, 1983, **105**, 4256, 5747.
[18] McGuire M., McLendon G., *J. Phys. Chem.*, 1986, **90**, 2549.
[19] Deisenhofer J., Epp O., Miki K., Huber R., Michel H., *J. Mol. Biol.*, 1984, **180**, 385.
[20] A discussion of this point is given in Haberkorn R., Michel-Beyerle M. E., Marcus R. A., *Proc. Natl. Acad. Sci. U.S.A.*, 1979, **76**, 4185.
[21] E.g., Denninger G., Dose V., Scheidt H., *Appl. Phys.*, 1979, **18**, 375; Woodruff D. P., Smith N. V., *Phys. Rev. Lett.*, 1982, **48**, 283, and references cited therein.
[22] Marcus R. A., *J. Chem. Phys.*, 1965, **43**, 1261.
[23] Marcus R. A., Sutin N., *Comments Inorg. Chem.*, 1986, **5**, 119; Hush N. S., *Electrochim. Acta*, 1968, **13**, 1005.
[24] Delahay P., Dziedzic A., *J. Chem. Phys.*, 1984, **80**, 5381, 5793, and references cited therein.